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ARTICLE

Bright Structural Coloration from Organic Polymeric Photonic Crystal with Robust Heat-Resistance

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Feihu Li,[a] Bingtao Tang,*[a] Suli Wu,[a] Wei Ma[a] and Shufen Zhang[a]

Organic polymeric microspheres, which can be easily synthesized through simple emulsion polymerization, are important building blocks of photonic crystal structural color materials. However, the poor heat resistance of organic polymeric photonic crystals is the intrinsic drawback that severely limits their practical application. In this study, novel polymeric photonic crystal structures with robust heat resistance are developed from the self-assembly of thiodiphenol-formaldehyde (TPF) microspheres. TPF microspheres with controllable particle size and high monodispersity are synthesized through polycondensation and cross-linking reaction between 4,4'-thiodiphenol and formaldehyde via a hydrothermal process. Derived from the highly cross-linked network structure and high content of aromatic rings and sulfur atoms of the TPF microspheres, the obtained polymeric photonic crystals exhibit bright structural colors and excellent heat resistance up to 250 °C. By contrast, general polystyrene photonic crystals possess poor heat resistance (<110 °C), due to the linear macromolecular structure. The distinct heat resistance feature of TPF structural colors is highly important for expanding their practical applications.

Introduction

Photonic crystals have attracted considerable attention because of their unique optical properties derived from the periodic modulation of the dielectric constant in regular colloidal arrays.[1-5] When the periodicity of the regular arrays is on the length scale about half the wavelength of visible light, structural colors can be generated, which are similar to natural opals.[6-12] A number of optical and color related applications have been demonstrated based on their unique structural color properties, such as in full color displays, colorimetric sensors, anticounterfeiting, photonic paper, coatings, and paints.[13-23] Moreover, polymeric colloidal photonic crystals are also widely used as colloidal templates towards inverse opal structures with various backbone materials.These applications require high stability of the photonic crystal structures to the surrounding environment and actual treatment condition.[24] Because, once the periodic photonic array is destroyed, their structural color will disappear irreversibly and the standard inverse opal structrures can not be obtained.[25] Particularly, the thermostability is a crucial feature for the potential applications in displays, coatings, photonic paper and colloidal templates, because the samples may suffer high temperature during solar radiation, electronic impact and CVD or PVD process.[26-30]

Among various artificial construction approaches of photonic crystals, the self-assembly of colloidal spheres, especially organic polymeric microspheres which can be easily synthesized by simple emulsion polymerization, is mostly utilized.[31-34] However, to date, the available monodispersed polymeric microspheres for constructing photonic crystals are mainly limited to polymethylmethacrylate (PMMA)[35-37] and polystyrene (PS).[38, 39] Their linear macromolecular structures and low glass transition temperature, which were ranges from 40 °C to 100 °C, lead to poor heat resistance of corresponding photonic crystals.[40] This intrinsic drawback of general organic polymeric photonic crystals severely limits their practical applications. Therefore, the development of new types of polymeric colloidal spheres that are suitable to construct photonic crystal structural color materials with distinct heat resistance is significantly important and urgently necessary.

In this paper, we report the synthesis of highly monodispersed thiodiphenol-formaldehyde (TPF) microspheres and their self-assembly to fabricate photonic crystals with robust heat resistance. The TPF microspheres were designed and synthesized through the polycondensation and cross-linking reaction between 4,4'-thiodiphenol and formaldehyde through a hydrothermal process. Controllable particle sizes (142-337 nm) and sufficient zeta potential (up to -35.4 mV) were realized. High-quality photonic crystals with bright and tunable structural colors were obtained from self-assembled TPF microspheres arrays. More importantly, the photonic crystal structures and structural colors exhibited robust heat resistance and thermal cycling stability (approximately 250 °C), which was derived from the internal high cross-linked network

[a] State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116024, China. *E-mail: tangbt@dlut.edu.cn

Electronic Supplementary Information (ESI) available: Large-scale SEM image of TPF spheres synthesized under the typical parameter; synthesis parameters and corresponding properties of TPF microspheres synthesized at different monomer concentration; digital photographs of red, orange and green TPF structural color flms; digital photographs of red, orange and green TPF structural color films heat-treated at different temperature and time; reflectance spectra of three TPF structural color films heat-treated at 300 °C for different time; TGA and DTG curves of the TPF microspheres sample. See DOI: 10.1039/x0xx00000x

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structure and aromatic rings of TPF microspheres. This unique feature is considerably important for their practical applications, such as in color displays, photonic paper, coatings and colloidal templates.

Experimental Section

Materials

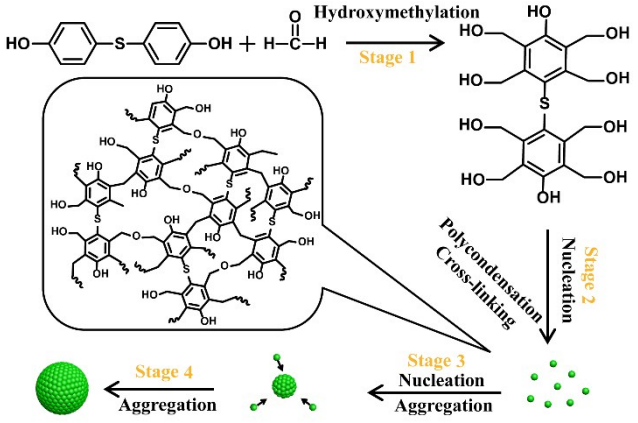
Formaldehyde solution (37 wt.%) and 4,4'-Thiodiphenol (98 wt.%) were purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). Triethylamine (TEA, 99 wt.%) and absolute ethanol were purchased from Sinopharm Chemical Reagent Co.,Ltd (Shanghai, China). Pluronic F-127 was purchased from Sigma Aldrich. All reagents were analytical grade and used as received. Deionized water was used in all experiments.

Synthesis of Monodispersed TPF Microspheres

Highly monodispersed TPF microspheres were synthesized through the polycondensation and cross-linking reaction between 4,4'-thiodiphenol and formaldehyde using F-127 as a surfactant through a hydrothermal process. In a typical synthesis process, 4,4'-thiodiphenol (0.225 g) was first dissolved in ethanol (20 mL) with vigorous magnetic stirring at room temperature (RT) and then mixed with water (50 mL) to obtain a clear solution. Subsequently, 0.05 g of F-127 was added, and the clear solution turned into milk white immediately. After stirring for 10 min, formaldehyde solution (0.225 mL) and triethylamine (TEA, 0.3 mL) were added to the reaction mixture and then stirred for another 10 min. Finally, the precursor solution was transferred into a Teflon-lined autoclave (100 mL) and then placed in an oven at 150 °C under static conditions. After 12 h of hydrothermal reaction, TPF microspheres dispersion was obtained. This original dispersion was separated and washed three times using water in centrifugation/redispersion cycles to remove impurity completely. Subsequently, pure TPF microspheres were ultrasonically redispersed in water.

Fabrication of Structural Color Films

Thermal assisted self-assembly method was used to prepare the structural color films, which was reported in our previous studies.[41, 42] Glass slides were used as substrate and were immersed in chromic acid lotion for 12 h and carefully washed and dried with N_2 before using.



Scheme 1 Schematic illustrating the formation process of monodispersed TPF microspheres.

Heat Resistance Testing of TPF Structural Color Films

To investigate their heat resistance property, the prepared TPF structural color films were placed in a muffle furnace that was pre-heated to the treating temperature for a certain time of heat treatment. Afterward, the samples were taken out and cooled to RT for testing.

Characterization

SEM images of the samples were obtained using a Nova NanoSEM 450 scanning electron microscope. All the samples were coated with gold before observation. TEM images were carried out with a FEI Tecnai G2 F30 microscope. Samples were prepared on a holey carbon film on a Cu grid. The particle hydrodynamic size and zeta potential were measured using a Zetasizer NanoZS-90 measurement system (Malvern instruments, Malvern, UK). Thermogravimetric analyses (TGA) were conducted with a TA Instruments Universal Analysis 2000. The reflection spectra were measured by HITACHI U-4100 spectrophotometer (HITACHI, Tokyo, Japan) at the scan speed of 300 nm/min and 5° incident angle. Digital photographs were taken by a Nikon D7000 digital camera.

Results and Discussion

Preparation and Characterization of TPF Microspheres

The TPF microspheres were synthesized through the polycondensation and cross-linking reaction between 4,4'-thiodiphenoland formaldehyde. As shown in Scheme 1, 4,4'-thiodiphenol possess multiple reactive sites that can react with formaldehyde to form hydroxymethyl–thiodiphenol in the initial reaction stage (Stage 1). Simultaneously, polycondensation and cross-linking reaction can easily occur among these hydroxymethyl groups, involving the formation of both methylene–ether and methylene bridges.[43-45]

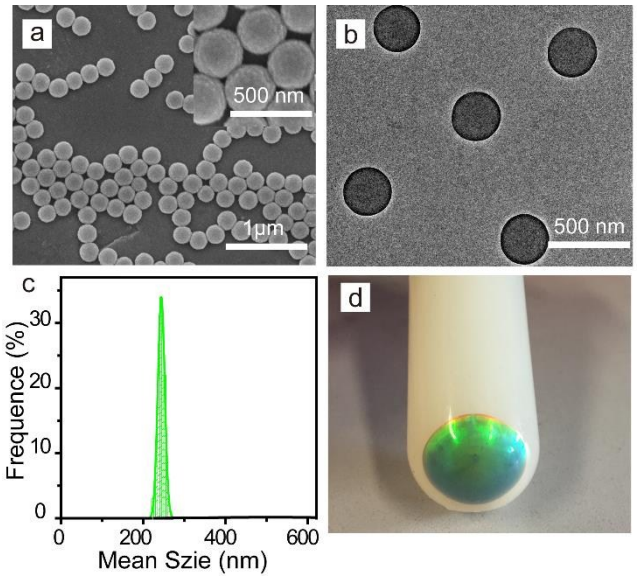


Fig. 1 a), b) SEM and TEM images of the synthesized TPF microspheres; c) Corresponding particle size distribution diagram; d) Photograph of the bright color after centrifugation of TPF microspheres.

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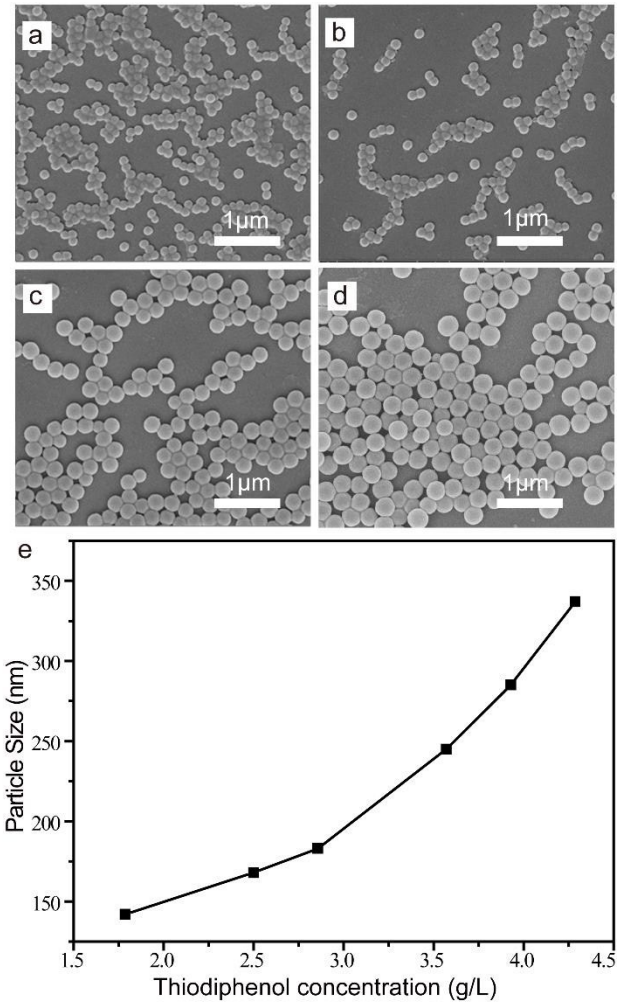

Fig. 2 a)-d) Typical SEM images of the monodispersed TPF microspheres synthesized at different initial thiodiphenol concentration: a) 1.78 g/L, b) 2.5 g/L, c) 3.93 g/L, and d) 4.28 g/L; e) Graph showing the relationship between the average particle size and initial thiodiphenol concentration.

Consequently, small initial nuclei consisted of highly cross-linked TPF resin macromolecules with 3D networked structures were formed (Stage 2). More nuclei were then continuously formed and aggregated into large colloidal spheres (Stage 3). Finally, monodispersed TPF microspheres were formed (Stage 4); such process is similar to the formation of RF and SiO_2.[46-48]

The typical TPF microspheres were synthesized by using 0.225 g of 4,4'-thiodiphenol, 0.225 mL of formaldehyde, 0.05 g of F127, 0.3 mL of TEA, 20 mL of ethanol, and 50 mL of water and undergoing a hydrothermal process at 150 °C for 12 h. Scanning electron microscope image (SEM, Fig. 1a and S1) demonstrate that the synthesized TPF microspheres possessed spherical morphology and highly uniform particle size. The TPF microspheres were well separated from each other, indicating their good monodispersity. The transmission electron microscope (TEM) image in Fig. 1b further indicated their good size uniformity and solid spherical structure. The particle average diameter was statistically calculated on the basis of counting 200 individual particles in the SEM images. The calculated result shows that the obtained TPF microspheres have an average diameter of 231 nm. The corresponding particle size distribution diagram in Fig. 1c also shows a narrow peak. The particle size distribution index from DLS measurement was 0.003. Moreover, the prepared TPF spheres can exhibit a bright and shiny structural color of green after centrifugation, as shown in Fig. 1d. These results further demonstrate that the obtained TPF microspheres are highly uniform in size and suitable building blocks of photonic crystals.

Particle Size Modulation of TPF Microspheres

According to Bragg's law, the accurate control of particle size is important to realize photonic crystals with tunable structural colors.[3, 49] During the experiments, the initial monomer concentration was a crucial factor that influenced TPF particle size. As shown in Fig. 2 and Table S1, the TPF average particle sizes can be precisely controlled from 142 nm to 337 nm when the initial 4,4'-thiodiphenol concentration was changed from 1.78 g/L to 4.28 g/L. Moreover, high particle size uniformity was maintained because a high monomer concentration indicated that more nucleis were formed in per unit volume to aggregate on the initial clusters and form larger final particles.

Moreover, the synthesized TPF microspheres showed sufficient negative surface charges. As shown in Table S1, the zeta potential of TPF colloidal dispersion was up to -35.4 mV. These negative surface charges can provide sufficient electrostatic repulsion, which is essential for the stabilization of the TPF colloidal dispersion. Such repulsion also endows the TPF microspheres with good self-assembly ability.

Heat Resistance Property of TPF Structural Color Films

Heat resistance is an important property that determines the practical application of photonic crystals. Thus, the heat

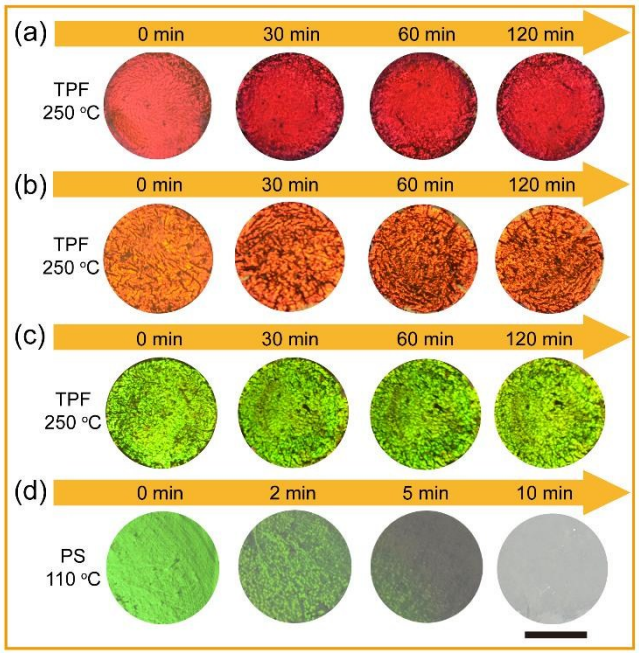

Fig. 3 Digital photographs of TPF and PS structural color films heat-treated at different temperature and time: a)-c) red, green , orange TPF structural color films under 250 °C; d) green PS structural color film under 110 °C; The scale bar is 1 cm.

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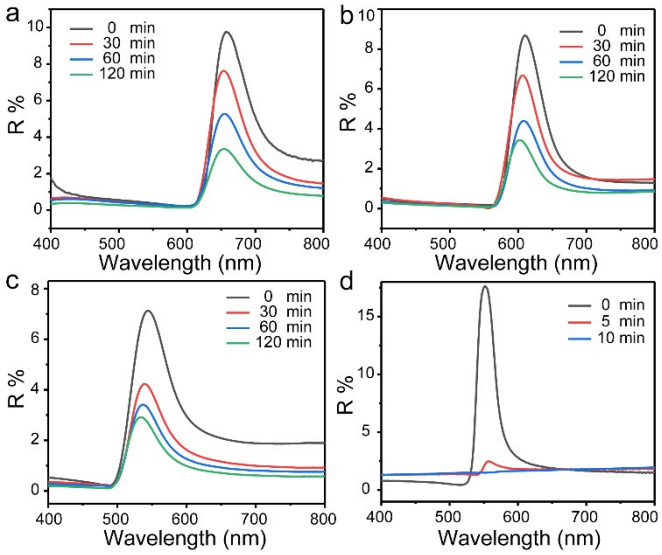

Fig. 4 a)-c) Reflectance spectra of the red, orange and green TPF structural color films heat-treated at 250 °C: a) red, b) orange and c) green; d) Reflectance spectra of the green PS structural color film heat-treated at 110 °C.

resistance property of TPF structural color films was studied in detail. First, three types of monodispersed TPF microspheres with an average particle diameter of 278, 265, and 231 nm were selected to fabricate structural color films. As shown in Fig. S2, three photonic crystal films with bright structural colors of red, orange, and green were obtained after the thermal-assisted self-assembly process. The diameter of all the circular structural color samples is 2 cm and the corresponding area is 3.14 cm^2.

Afterward, the TPF structural color films were placed in a muffle furnace for the heat treatment experiment. Fig. 3 shows the corresponding structural color photographs of TPF films heat treated under 250 °C and PS films heat treated under 110 °C for different time points. As can be seen in Fig. 3a, 3b, and 3c, the structural colors of the TPF structural color films that were heat treated at 250 °C for 0, 30, 60, and 120 min were undamaged by the high temperature and maintained their original colors. Moreover, their structural colors can be maintained even under 300 °C, despite the presence of a certain degree of damage and color change (Fig. S3, S4, and S5). By contrast, the PS structural color faded quickly with heat treatment at 110 °C (Fig. 3d), due to its low glass transition temperature.[40] These testing results directly demonstrate the robust heat resistance (up to 250 °C) of the TPF structural color films.

The heat resistance of TPF structural color films was further identified by measuring their reflectance spectra (Fig. 4). The reflectance spectra of red, orange, and green TPF structural color films only showed slight peak shifts at approximately 10, 8, and 8 nm after heat treatment at 250 °C for 120 min. Their corresponding reflectivity also remained at considerable levels (>3%). Consequently, these films showed bright colors (Fig. 3a, 3b, and 3c) despite undergoing a certain decrease of reflectivity compared with the original value. When the heating temperature was at 300 °C for 120 min, their peak positions showed remarkable blue shifts at about 36, 33, and 28 nm, but they still maintained a reasonable reflectivity and bright structural color (Fig. S6). By contrast, the reflectance peak of the PS structural color film completely disappeared under 110 °C heat treatment for 10 min (Fig. 4d).

SEM observation was carried out to determine the surface microstructure of the TPF structural color films. As shown in Fig. 5 (a-f), the TPF microstructures showed robust thermostability and maintained their original periodic structures at 250 °C. The corresponding statistical average particle size showed that the TPF microspheres exhibited shrinkage of 27, 23, and 21 nm for the red, orange, and green films; such shrinkage may be caused by the further condensation of internal hydroxymethyl groups and resulted in the slight blue shifts of the reflectance peaks. The PS microstructures before and after heat treatment are shown in Fig. 5g and 5h. The PS periodic microstructure is completely destroyed and disappeared under 110 °C, due to the

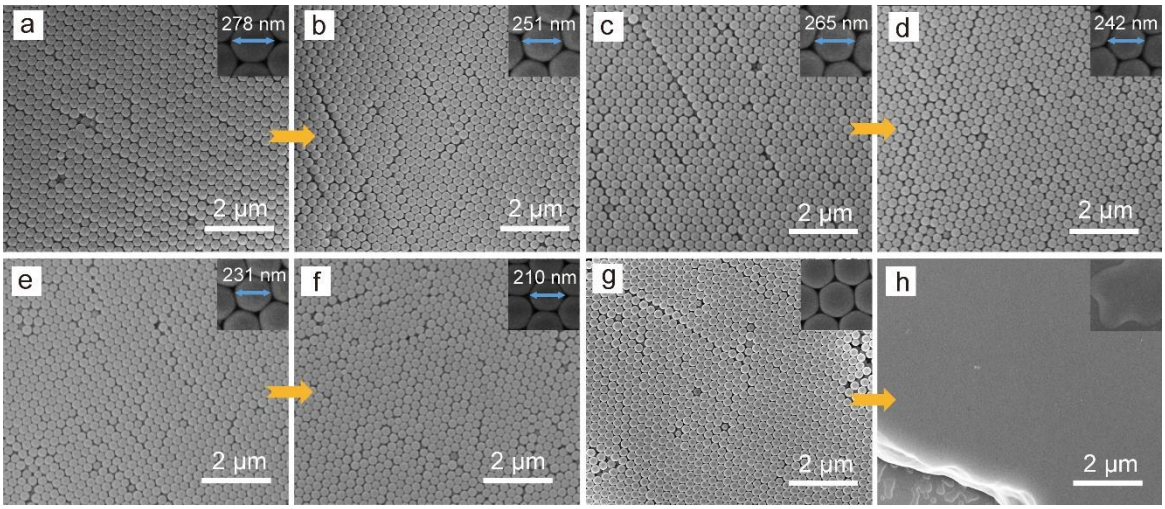

Fig. 5 a)-f) SEM images of the surface microstructure of three TPF structural color films before and afer heat-treatment at 250 °C for 120 min: a), b) red film; c), d) orange film; e), f） green film; g), h) SEM images of green PS structural color film before and afer heat-treatment at 110 °C.

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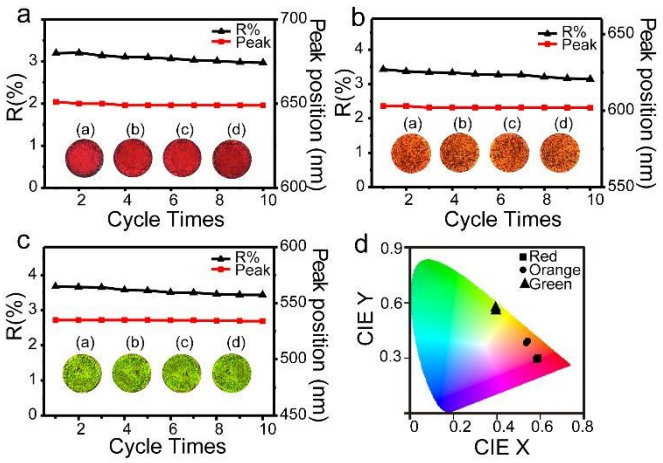

Fig. 6 a)-c) Thermal cycling curves of the reflection peak and reflectivity for red, orange and green TPF structural color films heat-treated under 250 °C; d) Corresponding CIE chromaticity diagram of the TPF structural color films at the 1st and 10th thermal cycling.

severely physical melting of the PS colloidal spheres, which resulted in the rapid structural color fading (Fig. 3d).

Thermal cycling experiments were carried out to evaluate the thermal cycling stability of the heat-treated TPF structural color samples. The samples were heat treated at 250 °C for 10 min very time for testing. The reflectance spectra of 10 cycling experiments demonstrate that the peak position and peak intensity had little change, as shown in Fig. 6a, 6b, and 6c. The corresponding chromaticity coordinate of the three structural colors almost remained at the same value and appeared in the same position in the CIE chromaticity diagram, as shown in Fig. 6d. These results further indicated the good thermal cycling stability of the TPF structural color films against 250 °C high temperature.

To explain the above experimental results, thermal gravimetric analysis (TG-DTG) was carried out on the TPF samples. As shown in Fig. S7, the TPF microspheres showed a weight loss of approximately 6.7% at 162 °C; this loss was attributed the internally adsorbed moisture and the further condensation of the residual hydroxymethyl groups,[46] which resulted in the decreased particle size and slight peak shifts. The TG and DTG curves (Fig. 7a and 7b) of the TPF microspheres that were pre-heat treated under 250 °C for different time points further indicated that the heat-treated TPF almost showed no weight loss between 100 °C and 250 °C, because the residual hydroxymethyl groups already reacted completely. These TGA-DTG results further confirmed the good thermostability of the TPF microspheres up to 250 °C. The thermostability was attributed to the internal highly cross-linked 3D networks of the TPF spheres that were generated from the polycondensation and cross-linking process and the exsitence of benzene ring. These highly cross-linked networks can act as rigid framework of the TPF microsphere. Thus, the TPF microspheres were endowed with good heat resistance and shape-stabilized property.

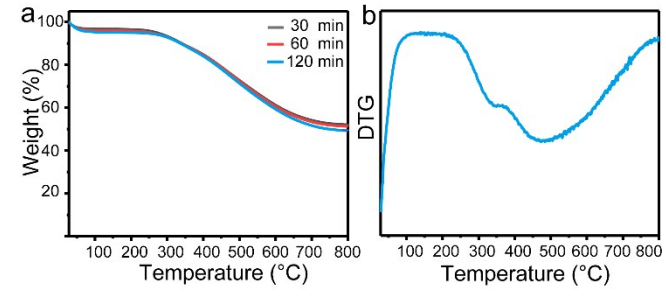

Fig. 7 a) TGA curves of TPF samples pre-heat treated under 250 °C for different time; b) DTG curve of the TPF sample treated under 250 °C for 120 min.

The good heat resistance of TPF colloidal crystal structures is significant for their application as candidate colloidal templates for preparing inverse opal structures. Because, the TPF colloidal templates can maintain their periodic structures during the filling of backbone materials through CVD or PVD process. The TPF templates can also be easily removed through high temperature decomposition, according to the TG-DTG measurement result in Fig. 7 and S7. Moreover,the good heat resistance of TPF colloidal spheres may also provide an opportunity for synthesizing monodispersed hard core-soft shell polymer composited particles and preparing opal structures through the melt-shear organization process, which involves the compression of the core-shell particles between the plates of a moderately hot press.[50-53]

Conclusions

Highly monodispersed TPF microspheres were designed and synthesized through the polycondensation and cross-linking reaction between 4,4'-thiodiphenol and formaldehyde. The average particle size can be precisely controlled within 142-337 nm, and their good monodispersity can also be maintained. The TPF microspheres were directly used as building blocks to construct high-quality photonic crystals with a large-scale ordered arrays. Bright structural colors were obtained from the highly ordered TPF photonic arrays. More importantly, the TPF structural color films exhibited robust heat resistance and thermal cycling stability against 250 °C high temperature, which were attributed to the internal particles' highly cross-linked 3D networks and aromatic rings. This study presented a new synthesis strategy for the preparation of phenolic-based microspheres and an effective approach to fabricate polymeric structural color materials with robust heat resistance, which is considerably significant for their practical applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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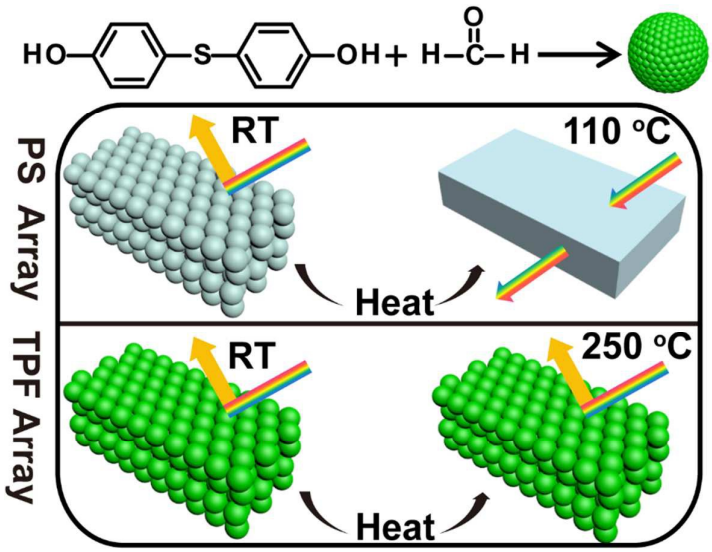

Polymeric photonic crystals with robust heat-resistance and bright structural color were constructed from self-assembled thiodiphenol-formaldehyde microspheres which possess cross-linked structure.

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